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(73) Proprietor: **SHELL INTERNATIONALE
RESEARCH MAATSCHAPPIJ B.V.
2596 HR Den Haag (NL)**

(72) Inventors:

- **Arnoldy, Peter**
1031 CM Amsterdam (NL)
- **Bolinger, Cornelis Mark**
Sugar Land, Texas 77478 (US)
- **Drent, Eit**
1031 CM Amsterdam (NL)
- **Keijsper, Johannes Jacobus**
1031 CM Amsterdam (NL)

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[0001] This invention relates to the hydroformylation of unsaturated hydrocarbons. In hydroformylation processes, carbon monoxide and hydrogen react with an olefinic feed to produce the corresponding hydroxymethyl-substituted or formyl-substituted derivative of the olefin. These processes are of great industrial importance in converting olefins to aldehydes and alcohols. Other products such as esters, acids, and amides can generally be prepared in analogous processes by adding the carbonyl moiety or the hydroxymethyl moiety to one of the carbon atoms situated at a double bond of the olefin.

[0002] EP-B 0 495 547 and US-A 5,488,174 describe a hydroformylation process which employs a catalyst system based on a source of palladium and a bidentate ligand of the formula $R_1R_2M_1RM_2R_3R_4$, in which M_1 and M_2 independently may be phosphorous, arsenic, or antimony atoms. R is a bivalent organic bridging group and R_1 , R_2 , R_3 and R_4 are unsubstituted or substituted aliphatic groups. One or more combinations of R_1 , R_2 , R_3 , and R_4 can form a bivalent cyclic group. These ligands can include, for example, a 1,2-bis(cyclooctylenephosphino) ethane (BCPE). According to US-A 5,488,174 a halide acts as a catalyst promoter in this process. According to US patent application SN 08/918,981 water acts as a co-promoter to the halide promoter.

[0003] The catalyst systems used in these processes typically employ strong acids as anion sources. Acids having a pKa of less than 3 (measured in aqueous solution at 18 °C) whose anions are non-coordinating or weakly coordinating with the metals of the platinum group have been found suitable for this purpose. Trifluoromethanesulphonic acid (TFMSA) has been the most preferred acid in this regard.

[0004] In the process described above, catalyst and promoter are added to a reactor charged with olefin, hydrogen, and carbon monoxide. The products, unreacted reactants, and catalyst are later separated by a solvent extraction technique typically utilizing a sulfolane/olefin/alcohol medium. The sulfolane cosolvent allows the catalyst to be separated and recycled via phase separation. Thus, the sulfolane is used as a phase-separating solvent.

[0005] Alternative separation methods might involve the use of solventless evaporative processes such as long tube vertical evaporators. The term "solventless" here refers to a distinction in the primary means by which separation occurs. A solventless evaporative process in this regard refers to a separation means in which one or more components of a liquor are separated primarily by virtue of their different boiling points. This is distinguishable from the reaction scheme identified above in which a sulfolane cosolvent facilitates the separation of liquor components by phase separation (i.e., as a function of solubility differences). Thus, a solvent-less evaporative separator process operates in the absence of a phase-separating solvent. The term does not mean that the reaction preceding the separation operates in the absence of any solvent. A hydroformylation process according to this invention could use any of a number of solvents to achieve purposes other than the primary facilitation of a separation of the products and/or intermediates involved in the process. For example, it could use olefins, alcohols and mixtures thereof.

[0006] Falling film evaporator (FFE) or wiped film evaporator (WFE) are examples of solventless evaporative separation means which find utility in industrial processes. Such separation methods take in liquids (such as the liquor leaving a reactor) at the top of a vertical evaporator arrangement. The liquid flows down the wall of the evaporator as a film and is heated. Lower boiling materials will separate out as vapour with the higher boiling liquid component collecting (and/or withdrawn) at the bottom. Many industrial processes are already equipped with this type of separation process. It can be advantageous to use a FFE or WFE when the material to be distilled is thermally sensitive because the contact time for the working fluid is significantly shorter in these devices.

[0007] The hydroformylation process of US-A 5,488,174 has not heretofore been readily workable with a solventless evaporative separation process such as may be conducted in a FFE. That is, such a process has not been found to be capable of separating the catalyst from the products and unreacted reactants leaving the reactor. The catalyst has tended to decompose at the high temperatures at which it is necessary to conduct the separation. Furthermore, it is often undesirable to employ a cosolvent such as sulfolane. Sulfolane has a boiling point which is often inconveniently close to or overlapping with the boiling range of many desirable product alcohols. At the very least, this requires an additional means to separate and recycle the sulfolane to the process.

[0008] There has now been found a catalyst composition which, besides being comparable in catalytic effectiveness to the best compositions under the above identified prior art, also has the advantage of being compatible with a solventless evaporative product separation system.

SUMMARY OF THE INVENTION

[0009] The present invention is a process for the hydroformylation of ethylenically unsaturated compounds with carbon monoxide and hydrogen in the presence of a catalyst system comprising

- a) a source of palladium, platinum, or nickel cations;
- b) a source of anions, other than halide anions;

c) a source of at least one bidentate ligands of the formula



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wherein M^1 and M^2 independently represent a phosphorus, arsenic or antimony atom, R represents a bivalent bridging group containing from 1-4 atoms in the bridge, R^1 and R^2 together represent a bivalent substituted or unsubstituted cyclic group whereby the two free valencies are linked to M^1 , and R^3 and R^4 independently represent a substituted or unsubstituted hydrocarbyl group, or together represent a bivalent substituted or unsubstituted cyclic group whereby the two free valencies are linked to M^2 ; and optionally
10 d) a promoter;

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wherein the catalyst system is chosen such that - when a)-c), taken in molecular ratios of 1:2:1, are slurried at ambient temperature and atmospheric pressure with a liquid mixture of the unsaturated compound feed and hydroformylated product taken in a volume ratio of 2:1 - said catalyst system is soluble to an amount of at least 2×10^{-4} mole of the cation a) per litre of said liquid mixture;

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and wherein the hydroformylation reaction products are separated from the catalyst system in a solventless evaporative separator.

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[0010] Examples of solventless evaporative separators are, as mentioned above, FFE and WFE.

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[0011] Examples of optional promoters d) are the chlorides, the iodides and the bromides. Preferably, water is added as a co-promoter.

DETAILED DESCRIPTION OF THE INVENTION

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[0012] In broad terms, the process of this invention is conducted by contacting an ethylenically unsaturated feed with carbon monoxide and hydrogen in the presence of the catalyst system and then separating reaction products from catalyst in a solventless evaporative separator.

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[0013] Examples of suitable cation sources a) for use in the catalyst system are platinum or palladium compounds such as salts of palladium and nitric acid, sulphuric acid or sulphonic acids, salts of platinum or palladium and carboxylic acids with up to 12 carbon atoms, palladium- or platinum complexes, e.g. with carbon monoxide or acetylacetone, or palladium combined with a solid material such as an ion exchanger or carbon. Palladium(II) acetate and platinum (II) acetylacetone are examples of preferred metal sources.

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[0014] Basically, the principle underlying the invention is that catalyst compositions of relatively low polarity are selected which will dissolve in the reaction system involved (feed used and product produced) to such a degree that they will remain in solution even in a solventless evaporative workout system. This principle can be satisfied in any or both of two ways, i.e. by selecting a suitable source of anions b) which is less polar than TFMMA and/or a suitable ligand c) which is less polar than BCPE. Notably, the combination of TFMMA (anion) and BCPE (ligand) in one catalyst composition, which combination according to the prior art is the combination of choice when the solvent extraction technique is used for product separation, is not effective when a solventless evaporative workout system is used and therefore it is not according to the present invention.

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[0015] As anion source b), any kind of compound generating these anions may be used. Suitably acids, or salts thereof, are used as source of anions, for example any of the acids mentioned above, which may also participate in the salts of the metals of the platinum group. Generally, anions of relatively low polarity are effective.

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[0016] Preferably, the source of anions b) has a pKa value of less than 3.

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[0017] Preferably, the anion source used in the catalyst composition according to the invention should have a boiling point, when measured at atmospheric pressure, of at least 50 °C above the boiling point of the hydroformylation product. More preferably the boiling point of the anion source is between 200 and 400 °C.

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[0018] Suitable anion sources include alkyl sulfonic acids such as methane sulfonic acid, ethane sulfonic acid, propane sulfonic acid and octane sulfonic acid; aryl sulfonic acids such as p-toluene sulfonic acid; perfluorinated alkyl sulfonic acids such as perfluoro octane sulfonic acid; perfluorinated aryl sulfonic acids such as pentafluoro benzene sulfonic acid; boric acid derivatives such as HBF_4 , $HB(C_6F_5)_4$ and alkylated versions thereof. These anion sources may also be used in conjunction with a Lewis acid such as BF_3 , $AlCl_3$, SnF_2 , $Sn(CF_3SO_3)_2$, $SnCl_2$ or $GeCl_2$ or a combination of a Lewis acid with an alcohol. This will result in the formation of a complex anion.

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[0019] Preferred anion sources are methane sulfonic acid (MSA), perfluoro octane sulfonic acid (PFOSA) and pentafluorobenzene sulfonic acid (PFBSA).

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[0020] In bidentate ligands c) in their skeletal form as broadly defined above, M_1 and M_2 are preferably the same and, more preferably, they are both phosphorus atoms, in which case the ligands are bisphosphines.

- [0021] The bridging group R is typically, though not necessarily, comprised of carbon atoms. It is preferred that they are C₂ or C₃ alkyl. Exemplary organic bridging groups are CH₂-CH₂ and CH₂-CH₂-CH₂.
- [0022] The bivalent cyclic group, represented by R₁ together with R₂, in general comprises at least 5 ring atoms and preferably contains from 6 to 9 ring atoms. More preferably the cyclic group contains 8 ring atoms. As a rule, all ring atoms are carbon atoms, but bivalent cyclic groups containing one or two heteroatoms in the ring, such as oxygen- or nitrogen atoms, are not precluded. Examples of suitable bivalent cyclic groups are 1,4-cyclohexylene, 1,4-cycloheptylene, 1,3-cycloheptylene, 1,2-cyclooctylene, 1,3-cyclooctylene, 1,4-cyclooctylene, 1,5-cyclooctylene, 2-methyl-1,5-cyclooctylene, 2,6-dimethyl-1,4-cyclooctylene and 2,6-dimethyl-1,5-cyclooctylene groups.
- [0023] Preferred bivalent cyclic groups are selected from 1,4-cyclooctylene, 1,5-cyclooctylene, and methyl (di)substituted derivatives thereof.
- [0024] Mixtures of ligands comprising different bivalent cyclic groups may be used as well, e.g. mixtures of ligands with 1,4-cyclooctylene and ligands with 1,5-cyclooctylene groups.
- [0025] R₃ and R₄ may independently represent various noncyclic or cyclic groups. Examples are alkyl groups such as ethyl, isopropyl, sec-butyl and tert-butyl groups, cycloalkyl groups such as cyclopentyl and cyclohexyl groups, aryl groups such as phenyl and tolyl groups and bivalent groups such as a hexamethylene group. Preferably, R₃, together with R₄ represents a bivalent cyclic group, in particular the same group as the group represented by R₁, together with R₂, in which case the two free valencies of the bivalent cyclic group are, of course, linked to M₂, instead of M₁. Thus, preferred bidentate ligands of formula (I) are 1,2-bis(1,4-cyclooctylenephosphino)ethane, 1,2-bis(1,5-cyclooctylenephosphino)ethane, their propane analogues, and mixtures thereof.
- [0026] In the process according to the present invention, ligands of relatively low polarity are preferred. Lower polarity can be achieved by selecting ligands in which the skeletal form as described above carries one or more non-polar substituents. These substituents can be placed on the skeletal bridging group R and/or on the bivalent cyclic group represented by R₁ and R₂ together, and/or on any of R₃ and R₄ when these are present separately, and/or on the bivalent cyclic group represented by R₃ and R₄ together, when present. The substituents, individually, may be alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl groups. They will preferably have from 1 to 30 atoms, one or more of which may be hetero-atoms such as oxygen or nitrogen.
- [0027] Bidentate ligands of this invention can be prepared in accordance with known techniques such as those disclosed in GB-A-1,127,965.
- [0028] The quantity of catalyst system used in the process of this invention may vary within wide limits. Usually amounts in the range of 10⁻⁸ to 10⁻¹, preferably in the range of 10⁻⁷ to 10⁻² mole atom of platinum group metal per mole of ethylenically unsaturated compound are used. The amounts of the participants in the catalyst system are conveniently selected such that per mole atom of platinum group metal from 0.5 to 10, preferably from 1 to 6 moles of bidentate ligand are used, and from 0.5 to 20, preferably from 1 to 8 moles of anion source or a complex anion source. It is more preferred that the process of this invention employs an anion to metal molar ratio of at least 2:1.
- [0029] It is preferred that the process of this invention is practised in the presence of a catalyst promoter. Halide anions are useful as promoters. Inorganic compounds including hydrogen halides such as HCl, HBr and HI may be used in this regard as well as metal halides such as NaCl, NaI, MgBr₂, ZnCl₂, ZnI₂, KBr, RbCl, CsCl, CsI, MgI₂ and CuCl. NaCl is the most preferred promoter.
- [0030] Another category of recommended sources of halide anions consists of halogen containing organic compounds which are capable of providing halide anions to the reaction medium. For example, organic phosphonium halides, such as triarylalkyl phosphonium chloride and halogen containing aromatic compounds such as 5-halobenzoic acids, e.g. 5-chlorobenzoic acid, 2,5-dichlorobenzoic acid, 2,3,5-tri-iodobenzoic acid, 3,5-di-iodobenzoic acid, m-halophthalic acids and esters thereof are all suitable.
- [0031] The molar ratio between halide anions and platinum group metal cations is preferably not more than 3:1. If larger amounts of halide anions are present, the activity of the catalyst system tends to be adversely affected, presumably because of coordination occurring between palladium and halide moieties. Preferably, the molar ratio between halide anions and platinum group metal cations is at most 2:1, more preferably less than 1:1, for instance from 0.02:1 to 1:1. The additional presence of water, in an amount of more than 0.6 wt% based on the total of the reaction mixture and up to its solubility limits under the reaction conditions, enhances the promoting effect of the halide promoter.
- [0032] The ethylenically unsaturated compound, used as starting material, is preferably an olefin having from 2 to 30 carbon atoms per molecule, or a mixture thereof. They may comprise one or more double bonds per molecule. Preferred are internal olefins having from 4 to 24 carbon atoms, or mixtures thereof. Such olefin mixtures are commercially available, for example as products of a process for the oligomerization of ethylene, followed by a double bond isomerization and disproportionation reaction. In the process of the invention, these internal olefins, usually mixtures of linear internal olefins with 6 to 20 carbon atoms per molecule, or closer boiling fractions of such mixtures, can be hydroformylated at high rates and an almost complete conversion. Examples are mixtures of linear internal C₆ to C₈ olefins, and of linear internal C₁₀ to C₁₄ olefins. Substituted olefins may also be used, for example unsaturated carboxylic acids, esters of such acids, or unsaturated esters of carboxylic acids, e.g. allylacetate. If desired, branched

olefins such as propene trimer or isomeric butene dimers (such as products of the well known "DIMERSOL" process) may be used, but the hydroformylation product will then, of course, contain branched structures as well. Olefinically unsaturated polymeric feedstock may also be used. This may include such materials as atactic polyolefins like 'Shube's' (mixture of oligomers of C₁₆-olefins), low molecular weight polyisobutylene (e.g., products commercially available from British Petroleum under the tradenames "NAPVIS" and "HYVIS"). Styrene-butadiene (block)copolymers may also be converted into interesting alcohols (as intermediates to synthetic lubricants, functionalized additives, etc.). Alpha-olefins, such as 1-octene and propene, and diolefins, such as norbornadiene, dicyclopentadiene, 1,5-hexadiene and 1,7-octadiene may also be used. The diolefins will of course yield (predominantly) a di-hydroformylated product, although mono-hydroformylated may also be formed.

[0033] Hydrogen and carbon monoxide may be supplied in equimolar or non-equimolar ratios, e.g. in a ratio within the range of 8:1 to 1:4, typically 4:1 to 1:2. Preferably they are supplied in a ratio within the range of 3:1 to 1:2.

[0034] In the process of the invention, the ethylenically unsaturated starting material and the formed hydroformylation product may act as reaction diluent. Hence, the use of a separate solvent is not necessary.

[0035] Nevertheless, the hydroformylation reaction may be carried out in the additional presence of a solvent if desired. The solvent may be useful in facilitating the reaction to form the products but will not be directed to facilitating the separation of liquor produced. For example, an anisole solvent can be combined with other catalyst components so that they are readily prepared in situ in the reaction scheme described above. For advantageous use of the FFE concept, codistillation of any solvent that is present with the product alcohol is generally not desired. In order to maintain a medium for the catalyst, it is desired that any such solvent be higher boiling than the product alcohol, so that a solution of catalyst in solvent remains after distillation of the product alcohol. In some cases with very high boiling product alcohol, this is a difficult attribute to satisfy. The solvent should also be inert to the catalyst components and thermally stable under distillation conditions. Examples of suitable solvents include malonitrile, 2-pyrrolidone, 1,5-pentanediol, dimethyl sulfoxide, and methyl terminated PEG.

[0036] The hydroformylation can be suitably carried out at moderate reaction conditions using reactors well known for their utility in hydroformylation processes. Temperatures in the range of 50 to 200 °C are recommended, preferred temperatures being in the range of 70 to 160 °C. Reaction pressures in the range of 500 to 10000 kPa are preferred. Lower or higher pressures may be selected, but are not considered particularly advantageous. Moreover, higher pressures require special equipment provisions.

[0037] Reaction products, by-products, unreacted reactants, and catalyst all leave the reactor as an effluent mixture according to this invention. They are then fed to a solventless evaporative separator. Exemplary of such evaporators are falling film evaporators (FFEs) and wiped film evaporators (WFEs). In the case of the FFE, which is the most preferred embodiment, the separator is heated by steam to between about 100 and 150 °C in the shell portion of the evaporator. In general, the falling film evaporator is a cylindrical apparatus with a heat source on the wall (the steam shell) and a cold surface in the middle of the cylinder. The product distils on the hot wall and condenses on the cold surface in the middle. The residence time of the effluent in the falling film evaporator is between about 5 seconds and 1 minute. For most product alcohols, it is satisfactory for the internal cooling surface to be a tube with cooling provided by means of circulating water. However, refrigerated media are also acceptable, especially when the product alcohol has a relatively low boiling point. A catalyst-containing liquid stream collects in the bottom of the separator. A weir at the bottom prevents mixing between the distilled product and the residual alcohol which contains the catalyst to be recycled. One or more additional conventional separation steps (such as distillations) may also be employed in this process as will be appreciated by one of ordinary skill in the art.

[0038] The process of the invention can be used for the preparation of alcohols from internal olefins at high rate, in particular by using a catalyst system as defined above, based on palladium as the platinum group metal.

[0039] Furthermore the process is very useful for the preparation of aldehydes having a high linearity, in particular by using a catalyst system as defined above, based on platinum as platinum group metal.

[0040] The invention will be illustrated by the following examples.

Examples

[0041] A rotary evaporator was used to simulate the use of a solventless evaporative separator. Indeed, it is most exemplary of a Falling Film Evaporator. A 500 ml stirred batch autoclave was used as a reactor. The catalyst solutions comprised a ligand formed from a mixture of 1,2-bis(1,4-cyclooctylenephosphino) ethane and 1,2-bis(1,5-cyclooctylenephosphino) ethane. These ligands are broadly representative of the class of organophosphine ligands described above. Catalyst solutions were formulated as follows:

| Catalyst | Pd Acetate (grams) | Ligand (grams) | Acid (grams) | Anisole (grams) |
|-----------------|--------------------|----------------|--------------|-----------------|
| A | 0.173 | 0.310 | 0.673 MSA | 19.9 |
| B (comparative) | 0.217 | 0.367 | 0.661 TFSA | 24.9 |
| C | 0.174 | 0.311 | 0.176 MSA | 20.0 |
| D | 0.0879 | 0.159 | 0.667 MSA | 19.9 |

MSA = Methanesulfonic Acid

TFSA = Trifluoromethanesulfonic Acid

[0042] In Examples 1-5, alcohols added to the feed were NEOFLEX 9, a brand isononanol commercially available from Shell Chemical Company, and NEODOL 23, a brand mixture of C₁₂-C₁₃ linear and branched alcohols available from Shell Chemical Company (NEOFLEX and NEODOL are trademarks).

[0043] The feed olefins used were C₈ isomerized butene dimer, made according to the DIMERSOL process and NEODENE 1112, a brand C₁₁-C₁₂ olefin mixture available from Shell Chemical Company (DIMERSOL and NEODENE are trademarks).

[0044] A 2:1 v/v mixture of NEODENE 1112 olefin and NEODOL 23 alcohol was slurried overnight at ambient temperature and atmospheric pressure with a composition of Pd acetate, MSA and ligand having the molar ratio of 1:2:1. Analysis by HPLC of a filtered sample taken from the slurry revealed that the amount of catalyst dissolved in the olefin/alcohol mixture corresponded to 0.0055 wt%, i.e. 3.67 × 10⁻⁴ mole, of palladium. Under the same conditions, when TFSA was used instead of MSA, the catalyst composition dissolves to an amount corresponding to less than 0.0005 wt%, i.e. 0.33 × 10⁻⁴ mole, of palladium. Thus, Catalyst B is not according to the present invention.

[0045] All percentages are on a weight basis unless otherwise indicated.

Example 1

[0046] The autoclave was charged with 71.2 g isononanol, 1.21 g water, 3.60 g of an aqueous sodium chloride solution which contained 0.0336 g sodium chloride, and 3.41 g n-decane (as an internal standard for gas chromatographic analysis of the product alcohol). Catalyst A was added to the content of the autoclave. After being flushed the autoclave was pressurised with hydrogen and carbon monoxide in a molar ratio of 2:1 to a pressure of 690 kPa and heated to 105 °C. The reaction was initiated by injecting 117.8 g C₈ isomerised olefin which was heated to 110 °C into the autoclave using additional hydrogen and carbon monoxide in a molar ratio of 2:1. The total pressure was 5200 kPa. Additional hydrogen and carbon monoxide in a molar ratio of 2:1 was automatically fed to the batch autoclave to replace the gas consumed in the reaction, maintaining a total pressure of 5200 kPa at all times.

[0047] Upon completion of the reaction the entire product mixture was distilled in a rotary evaporator which was heated to 130 °C. The overhead product contained virtually all of the anisole, water, n-decane, and unreacted octenes. The balance (up to 60% of the original reactor charge) was isononanol. The material remaining in the unevaporated product was isononanol and catalyst solution. It was determined by gas chromatographic analysis that 93.4% of the olefin had reacted. Of the olefin which reacted, 1.50% formed octane, less than 1% formed "heavy ends" which are predominantly acetals of isononanol and isononyl aldehyde, and the balance formed isononanol.

[0048] The unevaporated product (59.8 g) was returned to the batch autoclave. Water, 4.80 g, n-decane, 3.42 g, and isononanol, 30.0 g, was added to the autoclave which was then flushed with hydrogen and carbon monoxide in a molar ratio of 2:1 to a pressure of 690 kPa and heated to 105 °C. The reaction was initiated by injecting 136.3 g C₈ isomerised olefin. The reaction was completed as before, and the product was distilled. The overheads contained water, n-decane, and unreacted octenes. The balance (up to 60% of the original reactor charge) was isononanol. The material remaining in the unevaporated product was isononanol and catalyst solution. It was determined by gas chromatographic analysis that 93.4% of the olefin had reacted. Of the olefin which reacted, 1.52% on a molar basis formed octane, less than 1% formed "heavy ends" which are predominantly acetals of isononanol and isononyl aldehyde, and the balance formed isononanol.

[0049] The unevaporated product (98.5 g) was returned to the batch autoclave. Water, 4.80 g, n-decane, 3.42 g, and isononanol, 30.0 g, was added to the autoclave which was then flushed with hydrogen and carbon monoxide in a molar ratio of 2:1 to a pressure of 690 kPa and heated to 105 °C. The reaction was initiated by injecting 102.9 g C₈ isomerised olefin into the autoclave using additional hydrogen and carbon monoxide in a molar ratio of 2:1. The reaction was completed as before, and the product was distilled. The overheads contain water, n-decane, and unreacted octenes. The balance (up to 60% of the original reactor charge) was isononanol. The material remaining in the unevaporated product was isononanol and catalyst (palladium, organophosphine, methanesulfonic acid, hydrogen chloride, and sodium chloride). It was determined by gas chromatographic analysis that 93.6% of the olefin had reacted. Of the olefin

which reacted, 1.54% formed octane, less than 1% formed "heavy ends" which are predominantly acetals of isononanol and isononyl aldehyde, and the balance formed isononanol.

[0050] This sequence of hydroformylation and distillation reactions continued for 5 more cycles. The olefin conversions measured were 93.5, 93.2, 97.0, 92.6, and 86.8%. The paraffin formed in each cycle was 1.49, 1.66, 1.53, 1.49, and 2.42% molar. For the final iteration, heavy ends had accumulated to 2.7% by weight of the reactor product. There was no evidence of plating of palladium metal at the end of the 8 iterations, and elemental analysis confirmed that 100% of the expected palladium concentration was present in the solution.

[0051] The acid/Pd ratio (mole/mole) was 9 throughout the example.

[0052] This example illustrates that catalyst solution employing MSA as the anion source is robust, stable, and easily recoverable in a hydroformylation process employing a FFA. Further, the process results in very low make of paraffins and heavy ends.

Example 2

[0053] Example 1 was repeated except that the hydroformylation reactions were conducted at 110 °C. Upon completion of the first reaction it was determined by gas chromatographic analysis that 95.5% of the olefin had reacted. Of the reacted olefin, 0.6% formed octane, less than 1% formed "heavy ends" which were predominantly acetals and isononanol and isononyl aldehyde, and the balance formed isononanol.

[0054] This sequence of hydroformylation and distillation reactions continued for 4 more cycles. The olefin conversions measured were 94.6, 94.2, 93.2, and 92.5%. The paraffin formed in each cycle was 1.62, 1.51, 1.86, and 1.83% molar. For the final experiment, heavy ends had accumulated to 2.3% by weight of the reactor product. There was no evidence of plating of palladium metal at the end of the 5 experiments.

[0055] The acid/Pd ratio (mole/mole) was 9 throughout the example.

[0056] This example further illustrates that catalyst solution employing MSA as the anion source is robust, stable, and easily recoverable in a hydroformylation process employing a FFA. Further, the process results in very low make of paraffins and heavy ends.

Example 3 (Comparative)

[0057] The autoclave was charged with 89 g isononanol, 3.50 g water, 4.50 g of an aqueous solution of sodium chloride which contained 0.0419 g sodium chloride, and 4.21 g n-decane (as an internal standard for gas chromatographic analysis of the product alcohol). Catalyst B was added to the content of the autoclave. After being flushed the autoclave was pressurised with hydrogen and carbon monoxide in a molar ratio of 2:1 to a pressure of 690 kPa and heated to 105 °C. The reaction was initiated by injecting 149.2 g C₈ isomerised olefin into the autoclave using additional hydrogen and carbon monoxide in a molar ratio of 2:1. The total pressure was 5200 kPa. As in the example above, it was determined by gas chromatographic analysis that 95.4% of the olefin had reacted. Of the olefin which reacted, 1.25% formed octane, less than 1% formed "heavy ends" which are predominantly acetals of isononanol and isononyl aldehyde, and the balance formed isononanol.

[0058] This sequence of hydroformylation and distillation reactions continued for 2 more cycles. The olefin conversions measured were 96.2 and 95.8%. The paraffin formed in each cycle was 1.22 and 1.15%. Upon opening the autoclave after the third hydroformylation reaction, significant plating of palladium had occurred.

[0059] The organophosphine catalyst solutions were not robust and stable in the hydroformylation process employing a FFE when the catalysts employed TFSA as the anion source.

Example 4

[0060] The autoclave was charged with 71.2 g isononanol, 1.20 g water, 3.60 g of an aqueous solution of sodium chloride which contained 0.0336 g sodium chloride, and 2.93 g n-decane (as an internal standard for gas chromatographic analysis of the product alcohol). Catalyst C was added to the content of the autoclave. After being flushed the autoclave was pressurised with hydrogen and carbon monoxide in a molar ratio of 2:1 to a pressure of 690 kPa and heated to 105 °C. The reaction was initiated by injecting 119.5 g C₈ isomerised olefin into the autoclave using additional hydrogen and carbon monoxide in a molar ratio of 2:1. The total pressure was 5200 kPa. As in the example above, it was determined by gas chromatographic analysis that 91.2% of the olefin had reacted. Of the olefin which reacted, 1.25% formed octane, less than 1% formed "heavy ends" which are predominantly acetals of isononanol and isononyl aldehyde, and the balance formed isononanol.

[0061] This sequence of hydroformylation and distillation reactions continued for 4 more cycles. The olefin conversions measured were 90.5, 89.3, 87.4, and 83.3%. Upon opening the autoclave after the fifth hydroformylation reaction, significant plating of palladium had occurred, as confirmed by elemental analysis which revealed that 62% of the pal-

ladium had plated.

[0062] The acid/Pd ratio (mole/mole) was 2.3 throughout the example.

[0063] This example illustrates that the hydroformylation process employing the organophosphine/MSA catalyst solution described above should preferably have acid/Pd ratios of 2, and more preferably greater than 2.3 for long-term stability and viability of the process.

Example 5

[0064] The autoclave was charged with 71.2 g of NEODOL 23 brand alcohol; 0.60 g water, 1.80 g of a sodium chloride solution which contained 0.0168 g sodium chloride, and 3.38 g n-tridecane (as an internal standard for gas chromatographic analysis of the product alcohol). Catalyst D was added to the content of the autoclave. After being flushed the autoclave was pressurised with hydrogen and carbon monoxide in a molar ratio of 2:1 to a pressure of 690 kPa and heated to 105 °C. The reaction was initiated by injecting 119.88 g of NEODENE 1112 brand olefin which was heated to 110 °C into the autoclave using additional hydrogen and carbon monoxide in a molar ratio of 2:1. The total pressure was 5200 kPa. Additional hydrogen and carbon monoxide in a molar ratio of 2:1 was automatically fed to the batch

autoclave to replace the gas consumed in the reaction, maintaining a total pressure of 5200 kPa at all times. Upon completion of the reaction, the contents were removed, and the entire product mixture was distilled in a wiped film evaporator which was heated to 155 °C. The vacuum was adjusted so that approximately 60% by weight of the contents distilled overhead. This overhead product contained virtually all of the anisole, water, n-tridecane, and unreacted olefin.

The balance (up to 60% of the original reactor charge) was C12/13 alcohol with about 73% linearity. The material remaining in the unevaporated product was C12/13 alcohol and catalyst (palladium, organophosphine, methanesulfonic acid, hydrogen chloride, and sodium chloride). It was determined by gas chromatographic analysis that 99.6% of the olefin had reacted. Of the olefin which reacted, 0.75% formed paraffin, less than 1% formed "heavy ends", and the balance formed C12/13 alcohol.

[0065] The unevaporated product (100.0 g) was returned to the batch autoclave. It was determined by titration that a small portion of MSA had evaporated, so an additional 0.134 g MSA was added. Water (2.40 g), n-tridecane (3.40 g), and NEODOL 23 alcohol (44.4 g) was added to the autoclave which was then flushed with hydrogen and carbon monoxide in a molar ratio of 2:1 to a pressure of 690 kPa and heated to 105 °C. The reaction was initiated by injecting 90.2 g NEODENE 1112 mixed olefin which was heated to 110 °C into the autoclave using additional hydrogen and carbon monoxide in a molar ratio of 2:1. The reaction was completed as before, and the product was distilled in the wiped film evaporator. The overheads contained water, n-tridecane, and unreacted olefin. The balance (up to 60% of the original reactor charge) was C12/13 alcohol. The material remaining in the unevaporated product was C12/13 alcohol and catalyst (palladium, organophosphine, methanesulfonic acid, hydrogen chloride, and sodium chloride). It was determined by gas chromatographic analysis that 99.6% of the olefin had reacted. Of the olefin which reacted, 0.78% on a molar basis formed paraffin, less than 1% formed "heavy ends", and the balance formed C12/13 alcohol.

[0066] This sequence of hydroformylation and distillation reactions continued for 2 more cycles. The olefin conversions measured were 99.4% and 99.0%. The paraffin formed in each cycle was 0.72 and 0.98%. At the end of these reactions, a very small amount of plating was evident in the autoclave.

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Claims

1. A process for the hydroformylation of ethylenically unsaturated compounds with carbon monoxide and hydrogen in the presence of a catalyst system comprising:

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- a) a source of palladium, platinum, or nickel cations;
- b) a source of anions, other than halide anions;
- c) a source of at least one bidentate ligands of the formula



50 wherein M¹ and M² independently represent a phosphorus, arsenic or antimony atom, R represents a bivalent bridging group containing from 1-4 atoms in the bridge, R¹ and R² together represent a bivalent substituted or unsubstituted cyclic group whereby the two free valencies are linked to M¹, and R³ and R⁴ independently represent a substituted or unsubstituted hydrocarbyl group, or together represent a bivalent substituted or unsubstituted cyclic group whereby the two free valencies are linked to M²; and optionally

d) a promoter;

wherein the catalyst system is chosen such that - when a)-c), taken in molecular ratios of 1:2:1, are slurried at ambient temperature and atmospheric pressure with a liquid mixture of the unsaturated compound feed and hydroformylated product taken in a volume ratio of 2:1 - said catalyst system is soluble to an amount of at least 2 x 5 10^{-4} mole of the cation a) per litre of said liquid mixture;

and wherein the hydroformylation reaction products are separated from the catalyst system in a solventless evaporative separator.

- 10 2. A process according to claim 1, wherein the optional promoter d) is chosen from the group of chlorides, iodides and bromides, optionally with water as a co-promoter.
3. A process according to claim 1 or 2, wherein the source of anions b) has a pKa value of less than 3.
- 15 4. A process according to any one of claims 1 to 3, wherein the source of anion b) has a boiling point at atmospheric pressure which is at least 50 °C above the boiling point of the hydroformylation product.
5. A process according to claim 4, wherein the source of anions b) has a boiling point at atmospheric pressure of between 200 and 400 °C.
- 20 6. A process according to claim 5, wherein the source of anion is chosen from the group of alkyl sulfonic acids, aryl sulfonic acids, perfluorinated alkyl sulfonic acids, perfluorinated aryl sulfonic acids, boric acid derivatives and alkylated versions thereof.
- 25 7. A process according to claim 6, wherein the source of anions is chosen from the group of methane sulphonic acid, perfluoro octane sulphonic acid and pentafluoro benzene sulphonic acid.
8. A process according to any one of claims 4-7, wherein the bidentate ligand c) is 1,2-bis(cyclooctylenephosphino) ethane.
- 30 9. A process according to any one of claims 1-7, wherein the bidentate ligand c) carries on any of its groups R, R¹, R², R³ and R⁴ one or more non-polar substituents.
- 35 10. A process according to claim 9, wherein the substituent is chosen from the group of alkyl, cycloalkyl, aryl, alkylaryl and arylalkyl, one or more atom of which may be a hetero-atom.

Patentansprüche

40 1. Verfahren zur Hydroformylierung von ethylenisch ungesättigten Verbindungen mit Kohlenmonoxid und Wasserstoff in Gegenwart eines Katalysatorsystems, das die folgenden Komponenten umfaßt:

- a) eine Quelle für Palladium-Platin- oder Nickelkationen;
- b) eine Quelle für von Halogenidanionen unterschiedlichen Anionen;
- 45 c) eine Quelle für wenigstens einen Bitentatliganden mit der Formel



50 worin M¹ und M² unabhängig voneinander ein Phosphor-, Arsen- oder Antimonatom darstellen, R eine zweiwertige Brückengruppe mit 1 bis 4 Atomen in der Brücke bezeichnet, R¹ und R² zusammen eine zweiwertige substituierte oder unsubstituierte cyclische Gruppe deuten, wobei die beiden freien Valenzen an M¹ gebunden sind, und R³ und R⁴ unabhängig voneinander eine substituierte oder unsubstituierte Hydrocarbylgruppe darstellen oder gemeinsam eine zweiwertige substituierte oder unsubstituierte cyclische Gruppe bedeuten, wobei die beiden freien Valenzen an M² gebunden sind; und gegebenenfalls
55 d) eine Promotor;

wobei das Katalysatorsystem derart gewählt ist, daß dann, wenn a) bis c), eingesetzt in Molekularverhältnissen von 1:2:1, bei Umgebungstemperatur und atmosphärischem Druck mit einem flüssigen Gemisch aus dem Einsatzmaterial aus ungesättigter Verbindung und dem hydroformylierten Produkt, angenommen in einem Volumenverhältnis von 2:1, dieses Katalysatorsystem in einem Ausmaß von wenigstens 2×10^{-4} Mol des Kations a) pro Liter des genannten flüssigen Gemisches löslich ist;
 5 und worin die Hydroformylierungsreaktionsprodukte vom Katalysatorsystem in einem lösungsmittelfreien Verdampfungsseparator abgetrennt werden.

- 10 2. Verfahren nach Anspruch 1, worin der fakultative Promotor d) aus der Gruppe der Chloride, Jodide und Promide ausgewählt wird, gewünschtenfalls mit Wasser als Copromotor.
- 15 3. Verfahren nach Anspruch 1 oder 2, worin die Quelle für Anionen b) einen pKa-Wert von kleiner als 3 aufweist.
4. Verfahren nach einem der Ansprüche 1 bis 3, worin die Quelle für Anionen b) einen Siedepunkt bei Atmosphären-
 15 druck aufweist, der wenigstens 50°C über dem Siedepunkt des Hydroformylierungsproduktes liegt.
5. Verfahren nach Anspruch 4, worin die Quelle für Anionen b) einen Siedepunkt bei Atmosphärendruck zwischen
 20 200 und 400°C aufweist.
- 20 6. Verfahren nach Anspruch 5, worin die Quelle für Anionen aus der Gruppe der Alkylsulfonsäuren, Arylsulfonsäuren, perfluorierten Alkylsulfonsäuren, perfluorierten Arylsulfonsäuren, Borsäurederivaten und alkylierten Versionen hie-
 von ausgewählt wird.
- 25 7. Verfahren nach Anspruch 6, worin die Quelle für Anionen aus der Gruppe Methansulfonsäure, Perfluoroctansul-
 fonsäure und Pentafluorbenzolsulfonsäure ausgewählt wird.
8. Verfahren nach einem der Ansprüche 4 bis 7, worin der Bidentatligand c) 1,2-Bis(cyclooctylenphosphino)ethan ist.
- 30 9. Verfahren nach einem der Ansprüche 1 bis 7, worin der Bidentatligand c) auf einer seiner Gruppen R, R¹, R², R³
 und R⁴ einen oder mehrere nichtpolare Substituenten trägt.
10. Verfahren nach Anspruch 9, worin der Substituent aus der Gruppe Alkyl, Cycloalkyl, Aryl, Akylaryl und Arylalkyl,
 von denen ein oder mehrere Atome ein Heteroatom sein kann bzw. können, ausgewählt wird.

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Revendications

1. Procédé pour l'hydroformylation de composés éthyléniquement insaturés avec du monoxyde de carbone et de l'hydrogène en présence d'un système de catalyseur comprenant :
 40 a) une source de cations de palladium, platine ou nickel;
 b) une source d'anions, autres que des anions d'halogénure;
 c) une source d'au moins un ligand bidenté de la formule :

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dans laquelle M¹ et M² représentent indépendamment un atome de phosphore, d'arsenic ou d'antimoine, R représente un groupe de pontage bivalent contenant de 1-4 atomes dans le pont, R¹ et R² représentent ensemble un groupe cyclique substitué ou non substitué bivalent de sorte que les deux valences libres sont liées à M¹, et R³ et R⁴ représentent indépendamment un groupe hydrocarbyle substitué ou non substitué, ou bien ensemble représentent un groupe cyclique substitué ou non substitué bivalent de sorte que les deux valences libres sont liées à M²; et éventuellement
 55 d) un promoteur;

dans lequel le système de catalyseur est choisi de telle sorte que - lorsque a)-c), pris dans des rapports moléculaires de 1/2/1, sont délayés à la température ambiante et à la pression atmosphérique avec un mélange liquide

de l'alimentation en composé insaturé et du produit hydroformylé pris dans un rapport en volume de 2/1 - ledit système de catalyseur soit soluble en une quantité d'au moins 2×10^{-4} mole du cation a) par litre dudit mélange liquide;

5 et dans l quel les produits de réaction d'hydroformylation sont séparés du système de catalys ur dans un sépara-
rateur à évaporation sans solvant.

2. Procédé suivant la revendication 1, dans lequel le promoteur d) facultatif est choisi dans l groupe comprenant les chlorures, iodures et bromures, éventuellement avec de l'eau comme copromoteur.

10 3. Procédé suivant l'une ou l'autre des revendications 1 et 2, dans lequel la source d'anions b) a une valeur de pKa inférieure à 3.

15 4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel la source d'anions b) a un point d'ébullition à la pression atmosphérique qui est d'au moins 50°C au-dessus du point d'ébullition du produit d'hydroformylation.

5. Procédé suivant la revendication 4, dans lequel la source d'anions b) a un point d'ébullition à la pression atmos-
phérique entre 200 et 400°C.

20 6. Procédé suivant la revendication 5, dans lequel la source d'anions est choisie dans le groupe comprenant les acides alkyl sulfoniques, les acides aryl sulfoniques, les acides alkyl sulfoniques perfluorés, les acides aryl sulfo-
niques perfluorés, les dérivés d'acide borique et leurs versions alkylées.

7. Procédé suivant la revendication 6, dans lequel la source d'anions est choisie dans le groupe comprenant l'acide méthane sulfonique, l'acide perfluoro octane sulfonique et l'acide pentafluoro benzène sulfonique.

25 8. Procédé suivant l'une quelconque des revendications 4 à 7, dans lequel le ligand bidenté c) est le 1,2-bis(cyclooc-
tylène phosphino)éthane.

9. Procédé suivant l'une quelconque des revendications 1 à 7, dans lequel le ligand bidenté c) porte sur l'un quel-
conque de ses groupes R, R¹, R², R³ et R⁴ un ou plusieurs substituants non polaires.

30 10. Procédé suivant la revendication 9, dans lequel le substituant est choisi dans le groupe comprenant les groupes alkyle, cycloalkyle, aryle, alkylaryle et arylalkyle, dont un ou plusieurs atomes peuvent être un hétéroatome.

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